Comment on "Why Do Gallium Clusters Have a Higher Melting Point than the Bulk?"

The computational work [1], motivated by recent experiments [2] on the heat capacity measurements of small Ga_{39}^+ and Ga_{40}^+ clusters, claimed that the observed broad peak in the heat capacity represents melting of the small size clusters and made a strong point that due to the special character of the chemical bonds, these clusters, contrary to all expectations, melt at temperatures higher than the corresponding bulk material. In order to understand mysterious "higher-than-bulk melting temperatures" in small gallium clusters, Ga_{17} and Ga_{13}, they utilized the powerful machinery of the density functional theory (DFT) molecular dynamic (MD) simulations in a form of the isokinetic Born-Oppenheimer MD, using ultrasoft pseudopotentials within the LDA. The specific-heat curve, calculated by the multiple-histogram technique, indeed showed the peak in the heat capacity to be well above the bulk melting point of 303 K, viz., around 650 and 1400 K for Ga_{17} and Ga_{13}, respectively. The "higher-than-bulk melting temperatures" were attributed mainly to the covalent bonding in clusters, contrasting the covalent-metallic bonding in the bulk.

In our Comment we show that the peak in the heat capacity is in fact a well known generic behavior of finite size systems usually referred to as *Schottky anomaly.* Thus the connection of the peaks calculated in [1] (and also in the earlier works [3, 4]) to the real world is questionable.

The thermodynamic behavior of a finite system consisting of N particles is well discussed (as an exercise) in the R. Kubo textbook [5], Chapter 1, Example 4 on pages 38-41. When a system contains a substance having the excitation energy ΔE, the specific heat is given by the formula (9) of Example 4:

$$C = N k_B \left(\frac{\Delta E}{k_B T}\right)^2 \exp\left(\frac{\Delta E}{k_B T}\right) \Bigg/ \left(1 + \exp\left(\frac{\Delta E}{k_B T}\right)\right)^2 .$$

Shown in Figure 1 is the corresponding peak. The textbook exercise refers to the system of noninteracting particles. To see qualitatively what do interactions contribute to Schottky anomaly, one can consider, for example, a finite system of interacting spins. To avoid unnecessary complications we take the simplest analytically solvable model for a spin chain closed into the ring, i.e. the one-dimensional Ising model with the periodic boundary conditions [6]. The specific heat per spin

$$C = \frac{\partial}{\partial T}\left(\frac{k_B T^2}{N}\frac{\partial}{\partial T}\log(\lambda_+^N + \lambda_-^N)\right), \quad \lambda_\pm = e^{\frac{J}{k_B T}} \pm e^{\frac{-J}{k_B T}},$$

(J is the coupling constant) is shown in Figure 1. Note the shift of the position of the maximum to higher temperatures and growth of the maximum magnitude for the smaller cluster size exactly as presented in Figs. 4 and 5 of [1]. This kind of the size dependence is indeed typical for the Schottky anomaly. Interactions thus can only slightly change its shape, but the peak itself remains intact. This concludes our demonstration that the broad maximum in the heat capacity observed in [2] should be attributed rather to Schottky anomaly, than to cluster melting.

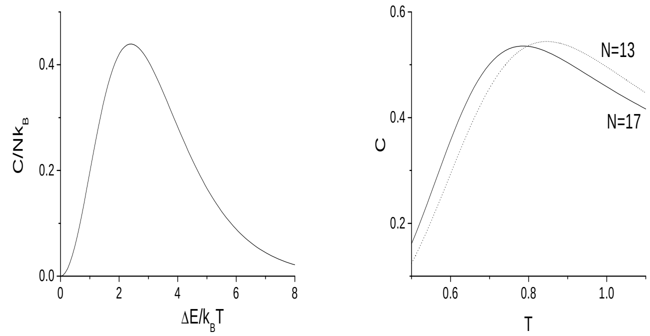

FIG. 1: Left: The Schottky specific heat. Figure 1.9 from [5]. Right: Specific heat C_V per spin of the Ising spin chain with $N = 17$ (solid line) and $N = 13$ (dotted line) spins.

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